



## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

## Process for Thinning Aqueous Inorganic Dispersions of Solids

We, HENKEL & CIE GMBH., a German Company, of 67, Henkelstrasse, 4000 Duesseldorf-Holthausen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for thinning aqueous inorganic dispersions of solids.

In practice it is desirable in many cases to bring about a "thinning" of aqueous inorganic dispersions of solids, such as slurries or drosses, that is, to lower the viscosity of the dispersions or to reduce their water content while keeping the viscosity the same. Such processes are used, for example, in the case of oil well liquids or slurries, the cleaning or processing of kaolin or china clay, ceramic drosses, rough cement slurries, slurries of montmorillonite or mica or aqueous pigment suspensions.

A number of additives for this purpose has already been proposed, but these have found only little acceptance in practice. Thus, numerous organic compounds have been proposed as additives for lowering the viscosity of mortar, concrete and cement mixtures, for example urea, lignin derivatives, phenolates, amino acids, amines, aliphatic and aromatic hydroxy-acids and polybasic organic acids or their salts. Relatively large additions of these substances are necessary, however, and they are not generally suitable for processes for thinning inorganic slurries, but only in special cases.

A further group of thinners comprises the alkali metal silicates, which are generally used in admixture with sodium carbonate or sodium hydroxide. The use of these products with slurries or silicates has the advantage that no foreign substances are introduced into the dispersions. Owing to their high content of alkali, however, they are not entirely satisfactory in practice and display undesirable side effects.

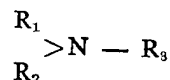
Thus they have an unfavourable effect on the texture of the solids obtained from the dispersions and, for example, in the case of ceramic bodies, lead to dark stripes or shadings at the edges of the solids. Furthermore, argillaceous slurries, when thinned with silicates, tend to produce undesirably high thixotropy.

Polyphosphates and organic phosphorus compounds form a further class of thinners, such, for example, salts of the acylation products of phosphorous acid and aminomethylene phosphonic acids. But these substances also have not been entirely satisfactory in practice. In aqueous dispersions the polyphosphates are known to be liable to hydrolysis, so that after a time their activity falls off and the dispersions thicken up again. The organic phosphorus compounds do not possess these undesirable effects, but in their case another undesirable side effect, which is also shown by the polyphosphates, occurs to a very special degree, that is, owing to their great dissolving power for alkaline earth compounds, the plaster of Paris moulds customary in ceramics technology are strongly attacked and quickly destroyed.

The use of a combination of salts of the acylation products of phosphorous acid and alkali metal silicates, which substantially reduce the faults described with reference both to the silicates and the organic phosphorus compounds has been proposed.

An object of the invention is to improve the known thinning agents.

According to the invention there is provided a process for thinning an aqueous inorganic dispersion of a solid which comprises adding a mixture of at least one alkali metal silicate and at least one water-soluble salt of an aminopolyphosphonic acid of the general formula

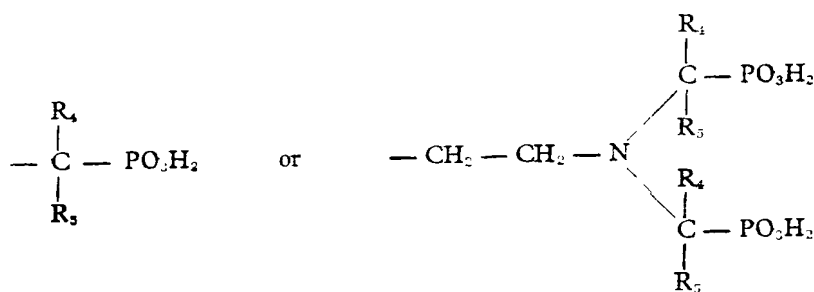


[Price 4s. 6d.]

to the aqueous inorganic solid dispersions in a quantity of 0.01 to 0.8% by weight, referred to the weight of the aqueous dispersions, and

wherein  $R_1$  and  $R_2$  in the above formula represent residues of the general formula

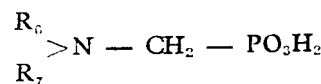
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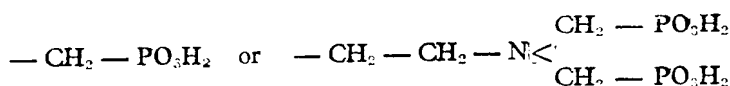
and  $R_1$  and  $R_2$  may be the same or different,  $R_3$  is the same as  $R_1$  or  $R_2$  or is a hydrogen atom, or an alkyl radical with 1 to 4 carbon atoms, or a hydroxyalkyl radical with 1 to 4 carbon atoms, and  $R_4$  and  $R_5$  represent hydrogen atoms or alkyl radicals with 1 to 4 carbon atoms, the proportions by weight of alkali metal silicate to aminopolyphosphonic acid salt in the mixture amounting to 20:1 to 2:1.

The usual water-soluble sodium or potassium silicates are preferably used as the alkali metal silicates. In the case of these silicates the proportion by weight of  $Me_2O:SiO_2$  may vary between 1:0.5 and 1:4.4,  $Me$  being an alkali metal. The silicates may be used both in solution and in solid form, and mixtures of different silicates may also be used.

Examples of aminopolyphosphonic acids which may be used include aminotri-(ethylidenephosphonic acid), ethylenediaminetetra-(ethylidenephosphonic acid), aminotri-(propylidenephosphonic acid), aminotri-(isopropylidenephosphonic acid), methylaminodi-(methylene-phosphonic acid), propylaminodi-(ethylidenephosphonic acid), and monoethanolaminedi-(methylene-phosphonic acid). Aminopolyphosphonic acids of the general formula



are preferred in which  $R_6$  and  $R_7$  represent residues of the general formula



and  $R_6$  and  $R_7$  may be the same or different, such as aminotri-(methylene-phosphonic acid), ethylenediaminetetra-(methylene-phosphonic acid) and diethylenetriaminepenta-(methylene-phosphonic acid).

Very good results are obtained with the commercially readily available aminotri-(methylene-phosphonic acid). Instead of single compounds, mixtures of several aminopolyphosphonic acids may also be used.

The aminopolyphosphonic acids are employed in the form of their water-soluble salts, preferably their alkali metal salts. The potassium and sodium salts have been found specially suitable. Instead of the salts, the free acids with addition of a corresponding amount of alkali may also be used.

The mixture of alkali metal silicate and aminopolyphosphonic acid contains the components in a proportion by weight of alkali metal silicate to aminopolyphosphonic acid salt of 20:1 to 2:1, preferably 10:1 to 3:1.

The mixture according to the invention is

added to the dispersions to be thinned in a quantity from 0.01 to 0.8%, preferably 0.05 to 0.5% by weight. The quantity depends upon the type of dispersion to be thinned and the fall in viscosity or reduction of water content desired. In most cases there are limiting values for the viscosity which are only further reduced by an insignificant extent even with considerably increased additions.

The mixtures of alkali metal silicate and aminopolyphosphonic acid may be added to the dispersion in solid form or in concentrated solution. The use of crystalline homogeneous mixtures is particularly advantageous. These solid, hydrated mixed crystallisates are obtained, for example, from the concentrated solutions of the components or when the dispersion of a corresponding anhydrous metasilicate in a concentrated aqueous solution of a salt of an aminopolyphosphonic acid is allowed to crystallise with formation of the corresponding hydrate of the silicate.

The mixture according to the invention dis-

plays a synergic action with respect to the thinning effect. The undesired side effects of the silicates and organic phosphorus compounds are reduced by the considerable reduction in concentration used due to the increased efficiency. In addition, the attack of the aminopolyphosphonic acid on the casting moulds is largely inhibited by the addition of silicate. Owing to the stability to alkali of the mixture according to the invention, the dispersions are stable over long periods without a change in viscosity taking place. The thixotropy occurring with higher degrees of thinning is surprisingly considerably reduced compared to the thinning obtained with the individual components.

The mixture according to the invention is superior in activity to other thinners, as the comparative experiments in the Examples given show. Owing to the very different nature of the inorganic materials and the individual dispersions, comparisons are only possible when a dispersion is used, which is absolutely the same in each case. Even in the case of dispersions known to be difficult to thin, a large reduction of viscosity is obtained by the mixture according to the invention, which remains unaltered over a long period.

The invention will be further illustrated by reference to the following Examples, in which percentages are by weight.

#### EXAMPLE 1.

To a finely ground fire clay mixture (pottery dross) with 70% content of solids and 30% water, which had a viscosity of about 22,000 centipoises, were added the following thinners according to the invention in the amounts indicated.

(a) Mixture of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and aminotri-(methylenephosphonic acid), pentasodium salt in the ratio 7.1:1.

(b) Mixed crystallisate of anhydrous  $\text{Na}_2\text{SiO}_3$ , pentasodium salt of aminotri-(methylenephosphonic acid), and water in the ratio 41.5:14:59.5.

(c) Mixed crystallisate of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and the pentasodium salt of aminotri-(methylenephosphonic acid) in the ratio 7.1:1, prepared from waterglass 58/60 Bé, NaOH, Water and aminotri-(methylenephosphonic acid).

The following known thinners were compared with the above:

(d)  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$

(e) Aminotri-(methylenephosphonic acid), penta sodium salt

(f) Mixture of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and the tetrasodium salt of hydroxyethanediphosphonic acid in the ratio 7.1:1.

The reductions in viscosity obtained by the above-named thinners are collected in Table 1. The viscosity measurements were carried out with a Brookfield viscometer.

TABLE 1

Thinner	% Thinner		
	0	0.10	0.125
(a)	ca. 22,000 cp	220 cp	120 cp
(b)	ca. 22,000 cp	170 cp	100 cp
(c)	ca. 22,000 cp	200 cp	105 cp
(d)	ca. 22,000 cp	—	2550 cp
(e)	ca. 22,000 cp	300 cp	280 cp
(f)	ca. 22,000 cp	1700 cp	180 cp

#### EXAMPLE 2.

To a china clay dross with 60% solids content and 40% of water, which had a viscosity of 20,000 centipoises, the following thinners were added in the amounts indicated.

(a) Mixture of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and the

pentasodium salt of aminotri-(methylenephosphonic acid), in the ratio 7.1:1.

(b) Mixture of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and the tetrasodium salt of hydroxyethanediphosphonic acid in the ratio 7.1:1.

(c)  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ .

TABLE 2

Thinner	% Thinner			
	0.05	0.10	0.125	0.20
(a)	14,750 cp.	4300 cp	2750 cp	2000 cp
(b)	16,000 cp	5500 cp	4200 cp	2800 cp
(c)	19,000 cp	—	11,500 cp	9000 cp

## EXAMPLE 3

A clay dross for highly durable material, which after an initial good thinning with a series of the usual thinners, such as quebracho, metasilicate, waterglass/soda, which showed a considerable rise in viscosity in a few hours, could be thinned from an initial viscosity of 25,000 cp to 1200 cp with 0.2% of a crystallisate from metasilicate and the pentasodium salt of aminotri-(methylenephosphonic acid) in the proportion by weight 7:1. No rise of the viscosity could be determined within a period of 3 weeks.

## EXAMPLE 4.

A clay dross (Amberger china clay) with a solid content of 70% and 30% of water was thinned with a mixed crystallisate which was prepared as follows:

100 parts by weight of waterglass  
58/60° Bé (27% SiO<sub>2</sub>, 18% Na<sub>2</sub>O)  
24 parts by weight of NaOH and  
21.4 parts by weight of water

were homogenised with 48.6 parts by weight of a 50% solution of the sodium salt of ethylenediaminetetra - (methylenephosphonic acid) at 40°C. On cooling to room temperature a dry grindable crystallisate was formed. The above-mentioned dross, which had a viscosity of about 24,000 cp, could be thinned to 136 cp by addition of 0.2% by weight of this product.

## EXAMPLE 5.

A clay dross, as in Example 4, with a viscosity of about 24,000 cp, was thinned to 1132 cp by addition of 0.2% by weight of a mixed crystallisate from waterglass and the sodium salt of monoethanolaminodi-

(methylenephosphonic acid), which was prepared in the same way as described in Example 4.

## EXAMPLE 6.

The same clay dross as in Example 4 could be thinned to viscosities from 120 to 1200 cp by the mixtures mentioned below when quantities between 0.1 and 0.3% by weight were added.

(a) Mixtures of potash waterglass 28/30° Bé (8.04% K<sub>2</sub>O, 20.38% SiO<sub>2</sub>) and the pentapotassium salt of aminotri-(methylenephosphonic acid) in the ratio 4:1.

(b) Mixed crystallisate from Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O and the sodium salt of diethylenetriamino-penta-(methylenephosphonic acid) in the ratio 6.6:1.

(c) Mixture of Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O and the sodium salt of aminotri-(isopropylenephosphonic acid) in the ratio 3.5:1.

(d) Mixed crystallisate from Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O and the sodium salt of ethylenediaminetetra-(ethylenephosphonic acid) in the ratio 9:1.

## EXAMPLE 7.

A dispersion of a fine calcium carbonate (prepared chalk) with 50% content of solids and 50% of water was treated with a mixed crystallisate according to Example 4 (Substance A) in increasing amounts and the decrease in viscosity was measured with a rotary viscometer.

For comparison, the same dispersion was treated with a mixed product according to Example 1 (f) (Substance B) and the decrease in viscosity was measured.

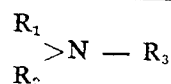
The results are given in Table 3.

TABLE 3

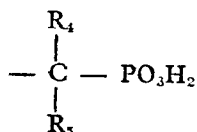
Thinner	% Thinner				
	0	0.1	0.3	0.4	0.5
Substance A	6560 cp	3250 cp	2350 cp	632 cp	248 cp
Substance B	6560 cp	—	—	1440 cp	708 cp

## WHAT WE CLAIM IS:—

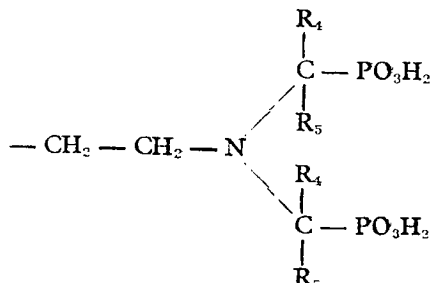
1. Process for thinning an aqueous inorganic dispersion of solids, which comprises adding to the dispersion a mixture containing at least one alkali metal silicate and at least one water-soluble salt of an aminopolyphosphonic acid of the general formula



in a quantity of 0.01 to 0.8% by weight, referred to the weight of the aqueous dispersions, in which formula  $R_1$  and  $R_2$  represent residues of the general formula



or

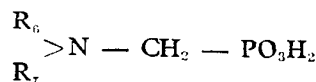


- and  $R_1$  and  $R_2$  may be the same or different,  $R_3$  is the same as  $R_1$  or  $R_2$  or a hydrogen atom, an alkyl radical with 1 to 4 carbon atoms or a hydroxyalkyl radical with 1 to 4 carbon atoms, and  $R_4$  and  $R_5$  represent hydrogen atoms or an alkyl radical with 1 to 4 carbon atoms, and the proportion by weight of alkali metal silicate to aminopolyphosphonic acid salt amounts to 20:1 to 2:1.

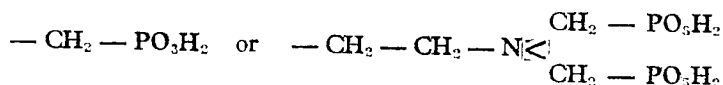
2. Process as claimed in claim 1, in which water-soluble sodium and/or potassium silicates with a proportion by weight of  $Me_2O$  to  $SiO_2$  between 1:0.5 and 1:4.4 are added

as alkali metal silicates,  $Me$  being an alkali metal.

3. Process as claimed in claim 1 or 2 in which the mixture contains at least one water-soluble salt of an aminopolyphosphonic acid of the general formula



in which  $R_6$  and  $R_7$  represent residues of the general formula



and  $R_6$  and  $R_7$  may be the same or different.

4. Process as claimed in any preceding claim in which the mixture contains a water-soluble salt of aminotri-(methylenephosphonic acid).

5. Process as claimed in any preceding claim in which the proportion by weight of alkali metal silicate to aminopolyphosphonic acid salt in the mixture amounts to 10:1 to 3:1.

6. Process as claimed in any preceding claim in which the mixture is added in a quantity of 0.05 to 0.5% by weight referred to the weight of the aqueous dispersions.

7. Process as claimed in any preceding claim in which a solid hydrated mixed crystal-

lisate of an alkali metal silicate and a salt of an aminopolyphosphonic acid is added to the aqueous inorganic dispersions of solids.

8. Process as claimed in any preceding claim in which the water soluble salt of an aminopolyphosphonic acid is an alkali metal salt.

9. Process as claimed in claim 1 substantially as hereinbefore described with reference to the foregoing Examples.

10. Aqueous inorganic dispersions of solids whenever obtained by a process as claimed in any preceding claim.

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